[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF BUFFALO]

STUDIES IN SILICO-ORGANIC COMPOUNDS. XXII. ALKOXYL AND AROXYL DERIVATIVES OF VINYLTRICHLOROSILANE

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DISCUSSION

The principle of the action of an alcohol on a chlorosilane is not new. Very few compounds, however, are to be found in the literature which have been prepared in this manner from vinyltrichlorosilane (1).

Vinyltrichlorosilane now has been shown to react with ethylene chlorohydrin (66.1% yield of product) and with allyl alcohol (64.8%) to form the corresponding vinyltrialkoxysilanes. Using simpler alcohols, vinyltriisoamoxysilane was prepared in 68.0% yield, vinyltricyclohexoxysilane in 66.7% yield, and vinyltriphenoxysilane in 61.7% yield. There is no significant difference between any of these figures. β-Methoxyethyl alcohol reacted with vinyltrichlorosilane to form vinyltris-(β-methoxyethoxy)silane in 46.0% yield. Three other compounds, homologs, were prepared—vinyltri-*n*-hexoxysilane, 66.5%; vinyltri-*n*-heptoxysilane, 52.9%; and vinyltri-*n*-octoxysilane, 43.4%.

tert-Butyl alcohol did not react with vinyltrichlorosilane to form any isolable product save a jelly-like polymer. The explanation has already been given (2). Undoubtedly, even in the presence of pyridine, some hydrochloric acid could form and react with the alcohol to give rise to water which could then act on the chlorosilane to form polymerized products.

Bromine reacted with vinyltriethoxysilane and diethylamine forming (probably) α-bromovinyltriethoxysilane. A second molecule of bromine added to the double bond. Bromine in methyl alcohol reacted with vinyltriethoxysilane to form bromovinyldiethoxymethoxysilane.

The probable positions of the bromine atoms in the above compounds have been given on the basis of the assumption that preliminary addition took place followed by loss of hydrobromic acid. It was believed that factors influencing and catalyzing *beta* elimination would operate to make *alpha*-bromine more stable than *beta*.

EXPERIMENTAL

Vinyltri-β-chloroethoxysilane. Anhydrous ethylene chlorohydrin (100 cc., 1.50 moles) was placed in the usual apparatus. Vinyltrichlorosilane (50.6 cc., 0.40 mole) was added slowly with stirring. The reaction proceeded easily. After complete addition of the silane, the reaction mixture was refluxed for 8 hours to drive off hydrogen chloride gas. Excess ethylene chlorohydrin was then removed at reduced pressure and the remainder of the liquid was further distilled with the isolation of vinyltri-β-chloroethoxysilane, b.p. 152.0–153.0° (6.5 mm.), n_D^{25} 1.4631, d_4^{25} 1.2462, 77.5 g., yield 66.1%.

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[1] A portion of the thesis presented by the first author as partial requirement for the degree of Doctor of Philosophy at the University of Buffalo.

Anal. Calc'd for $C_8H_{15}Cl_3O_3Si$: Cl, 36.23; Si, 9.57; M.R., 65.13.
Found: Cl, 36.23; Si, 9.58; M.R., 64.90.

Vinyltri-β-methoxyethoxysilane. In similar manner 79.0 cc. (1.0 mole) of β-methoxyethanol was treated with 38.0 cc. (0.3 mole) of vinyltrichlorosilane, with the isolation of vinyltri-β-methoxyethoxysilane, b.p. 136.2° (5.5 mm.), n_D^{25} 1.4271, d_4^{25} 1.0336, 38.6 g., yield 46.0%.

Anal. Calc'd for $C_{11}H_{24}O_6Si$: Si, 10.01; M.R., 69.81.
Found: Si, 9.97; M.R., 69.67.

Vinyltrialloxysilane. Anhydrous allyl alcohol (74.7 cc., 1.10 moles) was allowed to react with 44.4 cc. (0.35 mole) of vinyltrichlorosilane as outlined above. Vinyltrialloxysilane was isolated by distillation, b.p. 90.3° (7.5 mm.), n_D^{25} 1.4380, d_4^{25} 0.9455, 51.3 g., yield 64.8%.

Anal. Calc'd for $C_{11}H_{18}O_3Si$: Si, 12.40; M.R., 63.09.
Found: Si, 12.36; M.R., 62.84.

Vinyltrichlorosilane and tert-butyl alcohol. Anhydrous *tert*-butyl alcohol (94 cc., 1.00 mole), 81 cc. (1.00 mole) of anhydrous pyridine, and 38.0 cc. (0.30 mole) of vinyltrichlorosilane gave no isolable products save pyridine hydrochloride and a jelly-like polymer. The same results were obtained without the use of pyridine.

TABLE I

PHYSICAL PROPERTIES OF VINYLTRIALKOXYSILANES

COMPOUND	B.P., °C.	MM.	n_D^{25}	d_4^{25}
$CH_2{=}CHSi(OCH_2CH_2Cl)_3$	152.0–153.0	6.5	1.4631	1.2462
$CH_2{=}CHSi(OCH_2CH_2OCH_3)_3$	136.0	5.5	1.4271	1.0336
$CH_2{=}CHSi(OCH_2CH{=}CH_2)_3$	90.3	7.5	1.4380	0.9435
$CH_2{=}CHSi(OC_5H_{11}\text{-iso})_3$	136.8	6.0	1.4232	.8738
$CH_2{=}CHSi(OC_6H_{13}\text{-}n)_3$	177–179	7.5	1.4311	.8719
$CH_2{=}CHSi(OC_6H_{11})_3$	192–194	8.0	1.4378	.9956
$CH_2{=}CHSi(OC_7H_{15}\text{-}n)_3$	201–202	6.0	1.4335	.8706
$CH_2{=}CHSi(OC_8H_{17}\text{-}n)_3$	223–226	8.0	1.4390	.8639
$CH_2{=}CHSi(OC_6H_5)_3$	210.2	7.0	1.5617	1.1300
$CH_2{=}CBrSi(OC_2H_5)_3$[a]	77.6–77.9	5.5	1.4325	1.1990
$CH_2{=}CBrSi(OC_2H_5)_2OCH_3$[a]	73.7–75.0	6.0	1.4330	1.2219
$CH_2BrCBr_2Si(OC_2H_5)_3$[a]	143.1–143.5	7.0	1.4905	1.6637

[a] Position of halogens, "probable."

Vinyltriisoamoxysilane. Anhydrous isoamyl alcohol (125 cc., 1.15 mole) was caused to react with 44.4 cc. (0.35 mole) of vinyltrichlorosilane as above. Vinyltriisoamoxysilane was isolated, b.p. 136.8° (6.0 mm.), n_D^{25} 1.4232, d_4^{25} 0.8738, 75.2 g., yield 68.0%.

Anal. Calc'd for $C_{17}H_{36}O_3Si$: Si, 8.87; M.R., 92.28.
Found: Si, 8.87; M.R., 92.26.

Vinyltri-n-hexoxysilane. In similar manner, 138 cc. (1.10 mole) of *n*-hexyl alcohol was allowed to react with 44.4 cc. (0.35 mole) of vinyltrichlorosilane forming vinyltri-*n*-hexoxysilane, b.p. 177–179° (7.5 mm.), n_D^{25} 1.4311, d_4^{25} 0.8719, 83.5 g., yield 66.5%.

Anal. Calc'd for $C_{20}H_{42}O_3Si$: Si, 7.83; M.R., 106.17.
Found: Si, 7.92; M.R., 106.48.

Vinyltricyclohexoxysilane. Similarly, from cyclohexanol (105 cc., 0.99 mole) and vinyltrichlorosilane (31.7 cc., 0.25 mole) of vinyltricyclohexoxysilane was isolated, b.p. 192–194° (8.0 mm.), n_D^{25} 1.4738, d_4^{25} 0.9956, 70.5 g., yield 66.7%.

Anal. Calc'd for $C_{20}H_{36}O_3Si$: Si, 7.96; M.R., 99.78.
Found: Si, 7.83; M.R., 99.48.

Vinyltri-n-heptoxysilane. Anhydrous *n*-heptanol (142 cc., 1.0 mole) reacted similarly with 38.0 cc. (0.3 mole) of vinyltrichlorosilane. Vinyltri-*n*-heptoxysilane was isolated, b.p. 201.0–202.0° (6.0 mm.), n_D^{25} 1.4355, d_4^{25} 0.8706, 63.7 g., yield 52.9%.

Anal. Calc'd for $C_{23}H_{48}O_3Si$: Si, 7.00; M.R., 120.06.
Found: Si, 7.04; M.R., 120.21.

Vinyltri-n-octoxysilane. Anhydrous *n*-octyl alcohol (190 cc., 1.20 mole) was allowed to react, as above, with 44.4 cc. (0.35 mole) of vinyltrichlorosilane, with the isolation of vinyltri-*n*-octoxysilane, b.p. 223–226° (8.0 mm.), n_D^{25} 1.4390, d_4^{25} 0.8689, 67.0 g., yield 43.3%.

Anal. Calc'd for $C_{26}H_{54}O_3Si$: Si, 6.34; M.R., 133.95.
Found: Si, 6.38; M.R., 134.03.

Vinyltriphenoxysilane. Anhydrous phenol (176 g., 1.87 moles) was allowed to react without solvent, with 63.3 cc. (0.5 mole) of vinyltrichlorosilane as described above. Vinyltriphenoxysilane was isolated, b.p. 210.2° (7.0 mm.), n_D^{25} 1.5617, d_4^{25} 1.1300, 103 g., yield 61.7%.

Anal. Calc'd for $C_{20}H_{18}O_3Si$: Si, 8.39; M.R., 95.55.
Found: Si, 8.34; M.R., 95.93.

α-Bromovinyltriethoxysilane. Vinyltriethoxysilane (58.0 g., 0.32 mole) was placed in the usual apparatus. Bromine (15.6 cc., 0.32 mole) was added slowly with stirring. After complete addition of the bromine, the reaction mixture was heated gently with stirring for one hour. Diethylamine (38.1 cc., 0.37 mole) was added slowly with cooling in an ice-water bath. A dense white precipitate formed. The mixture was refluxed for four hours with stirring followed by the separation of the diethylammonium bromide. Excess diethylamine was removed at atmospheric pressure and the remainder of the liquid was further distilled at reduced pressure with the isolation of bromovinyltriethoxysilane (probably *alpha*), b.p. 77.6–77.9° (5.5 mm.), n_D^{25} 1.4325, d_4^{25} 1.1990, 28.5 g., yield 33.1%.

Anal. Calc'd for $C_8H_{17}BrO_3Si$: Si, 10.42; Br, 29.69; M.R., 58.29.
Found: Si, 10.58; Br, 29.65; M.R., 58.34.

Bromovinyldiethoxymethoxysilane. The above experiment was repeated using 55 g. of vinyltriethoxysilane and 13.8 cc. of bromine in 12.2 cc. of anhydrous methyl alcohol. Bromovinyldiethoxymethoxysilane was isolated, b.p. 73.7–75.0° (6.0 mm.), n_D^{25} 1.4330, d_4^{25} 1.2219, 8.0 g., yield 11%.

Anal. Calc'd for $C_7H_{15}BrO_3Si$: Si, 11.00; Br, 31.32; M.R., 53.66.
Found: Si, 10.98; Br, 31.25; M.R., 54.27.

Tribromoethyltriethoxysilane. Bromovinyltriethoxysilane (33.4 cc., 0.15 mole) was placed in the usual apparatus. Bromine (7.4 cc., 0.15 mole) was added rapidly with stirring. After complete addition of the bromine the reaction mixture was heated gently with stirring for three hours. Fractional distillation yielded (probably) α,α,β-tribromoethyltriethoxysilane, b.p. 143.1–143.5° (7.0 mm.), n_D^{25} 1.4905, d_4^{25} 1.6637, 28.7 g., yield 44%.

Anal. Calc'd for $C_8H_{17}Br_3O_3Si$: Si, 6.54; Br, 55.89; M.R., 74.12.
Found: Si, 6.59; Br, 56.17; M.R., 74.62.

Materials. Vinyltrichlorosilane was made available through the courtesy of the Linde Air Products Co. Other materials were purchased from equally reputable sources and found to possess satisfactory physical constants.

Vinyltriethoxysilane was prepared in accordance with the method of Nagel, Tamborski, and Post (1). Its physical constants were in satisfactory agreement with published values.

Analyses. Silicon and *bromine* were determined in accordance with methods already in the literature (3).

SUMMARY

1. Eight aliphatic alcohols (ethylene chlorohydrin, β-methoxyethyl, allyl, isoamyl, *n*-hexyl, cyclohexyl, *n*-heptyl, and *n*-octyl) as well as phenol, have been found to react with vinyltrichlorosilane to form compounds of the type $CH_2{=}CHSi(OR)_3$.

2. Vinyltriethoxysilane reacts with bromine and diethylamine with ultimate substitution of one hydrogen by bromine. A second molecule of bromine adds forming (probably) α,α,β-tribromoethyltriethoxysilane. Bromine in methyl alcohol reacts similarly but with replacement of one ethoxyl by methoxyl.

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BIBLIOGRAPHY

(1) NAGEL, TAMBORSKI, AND POST, *J. Org. Chem.*, **16**, 1768 (1951).
(2) BOYE AND POST, *J. Org. Chem.*, **16**, 391 (1951).
(3) NAGEL AND POST, *J. Org. Chem.*, **17**, paper XXI, this issue (1952).